

Thermodynamic study of characteristics of the converter with separated supply of hydrocarbon fuel for thermo-oxidative and steam reforming

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Thermodynamic studies of the converter characteristics were performed to produce hydrogen-containing syngas from hydrocarbon fuel (kerosene) with its separated supply for thermo-oxidative and steam reforming. It is demonstrated that the optimal conditions of the converter performance correlate with the oxidant ratio of $\alpha > 0.5$ at the heat-transfer wall temperature of 1200 K. Hydrogen content in the final syngas reaches 60 % by volume, free carbon (soot) deposition in reforming products is excluded, and there is no need to apply walls water cooling in the converter.

Key words: converter, hydrogen-containing syngas, kerosene, thermo-oxidative reforming, steam reforming, separated supply of fuel for reforming, reactor, heat-transfer wall, thermodynamic study.

Today, there is considerable interest in hydrogen utilization as an engine fuel. However, in spite of the positive properties of hydrogen, such as high calorific capacity, high combustion rate, and wide ignition range, especially toward lean mixtures, hydrogen features a number of disadvantages which prevent its practical application as an engine fuel. Among these disadvantages, above all, there is low density which is (in the liquid hydrogen at -253°C) just 70.8 kg/m^3 . At the same time, hydrogen is one of the most explosive and inflammable substances. Moreover, because of its extremely high fluidity it is very inconvenient to store.

In spite of above listed negative attributes, hydrogen turned out to be an irreplaceable fuel to be utilized either pure or mixed with other components for new promising power plants. For example, it is feasibly impossible to avoid hydrogen when realizing the stable process of supersonic combustion in scramjet combustion chambers for designed hypersonic aircraft [1–7].

Hydrogen added to hydrocarbon fuels supplied in combustion chambers of gas-turbine engines, both transport and stationary ones, permits not only increasing the fuel combustion efficiency but also reduce essentially the concentration of toxic components, such as nitrogen oxides NO_x , carbon oxide CO, hydrocarbons like CH and soot which is an active adsorbent of carcinogens, in exhaust gases [8].

The other important direction of investigations in the field of hydrogen power engineering is utilization of hydrogen in fuel elements which are nowadays applied in various transport

types and in industry. Intensive activity in this area in different countries is proven by the development of fuel elements and power plants with them which are demonstrated every year in the Hanover Fair, Germany [9].

Unfortunately, utilization of pure hydrogen at its long-term storage, especially for transport, is practically unrealizable. That is why hydrogen should be produced from hydrocarbon fuel without storage stage, directly in field. This process presents the engine fuel conversion, i.e., chemical transformation of hydrocarbons in the mixture of hydrogen-containing components. Conversion efficiency depends on the energy consumptions for its realization, and on hydrogen content in the produced syngas. Known conversion techniques are limited by two basic processes, namely the thermo-oxidative [10, 11, 12] and steam [13, 14] reforming. When using these processes in practice, a complex engineering problem has to be solved, both in the steam reforming of hydrocarbons, which requires supplying considerable quantity of heat, and in the case of thermo-oxidative reforming, which, on the contrary, needs heat withdrawal. Normally this problem is solved by means of the auto-thermal reforming which presents the combination of both aforesaid processes [15].

Specialists of RSC "Applied Chemistry" have been dealing with experimental and theoretical investigations of the steam and thermo-oxidative reforming of hydrocarbon fuels for a long time. These activities are purposed to the creation of a converter which could provide the chemical transformation of the hydrocarbon fuel in the syngas with the maximum achievable hydrogen content at the minimal possible heat losses into the ambient medium. Obtained results gave the base to develop the model of the converter with the separated fuel supply for the thermo-oxidative and steam reforming; this system permits improving significantly the performance of this converter as compared to the ones used today.

The proposed converter model with the separated supply of kerosene, when one part passes through a sprayer head 1 for the thermo-oxidative reforming and the other goes through the evaporator channel 7 for the steam reforming (Fig. 1). The heat in this converter needed for the steam reforming is supplied into the reactor 3, filled with a catalyst from the combustion chamber 4 through its heat-transfer wall, whereas kerosene and water come into the reactor as a steam mixture overheated up to minimum 573 K. The heating, evaporation, and overheating of these components occurs in the slit evaporator channel 7, wherein partially heated water comes from the sprayer head cooling jacket 2. The heat for water and fuel evaporation is supplied through the internal wall of the evaporator 7 from the area of mixing of thermo-oxidative and steam reforming products 6.

To choose the optimal relationship between the thermo-oxidative and steam reforming, as well as to determine the conditions of these processes realization, thermodynamic studies were carried out in order to evaluate the expected characteristics of the converter under consideration.

When performing thermodynamic calculations of the thermo-oxidative conversion, the following basic assumptions were used:

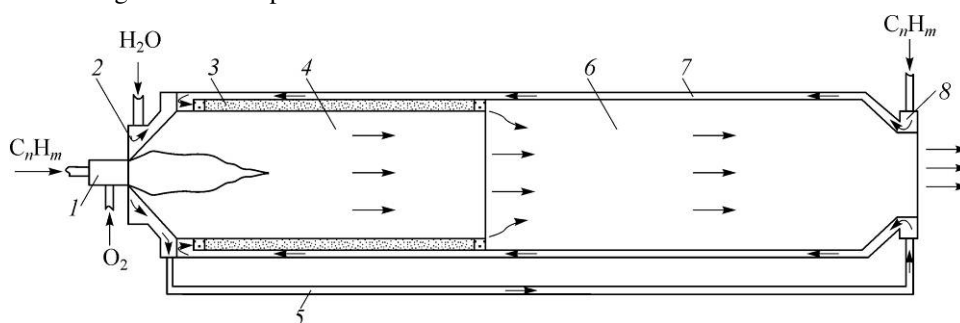


Fig. 1. Converter schematic.

1 — injector head, 2 — injector head cooling jacket, 3 — steam reforming reactor, 4 — converter combustion chamber, 5 — water feed line from the injector head into evaporator, 6 — area of mixing of thermo-oxidative and steam reforming products, 7 — slit channel of water and hydrocarbon fuel evaporator, 8 — mixer of water and hydrocarbon fuel coming into the evaporator.

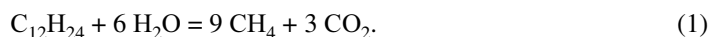
– it was assumed that the conversion products were mixed ideally and were in the chemical equilibrium state;

– the conversion products composition was presumed to be the pressure and temperature function at any point of the reactive mixture.

The calculation reduced to the solution of the non-linear algebraic system of equations including the material-balance equations for chemical elements of the initial mixture, equilibrium equations for reaction in accordance with the law of mass action by Guldberg and Waage, and the equation for the total pressure of the mixture which is equal to the sum of partial pressures of individual components (Dalton's law). The gas pressure in the converter combustion chamber was assumed to be 20 atm. The program complex developed in RSC "Applied Chemistry" was used to perform the thermodynamic calculations. The empirical formula $C_{12}H_{24}$, frequently applied for theoretical investigations, was used for kerosene.

Steam reforming investigation suggested the two-stage process. The first one starts and ends within the section from the fuel and water injection into the tail part of the converter up to the obtained products appearance in the slit reactor filled with the catalyst. The second, highly endothermic stage takes place in this reactor; it dictates the temperature regime of the performance of the converter combustion-chamber heat-transfer wall.

The first stage is described with the equation



From this equation it follows that utilization of 1 kg $C_{12}H_{24}$ results in 0.8571 kg CH_4 and 0.7857 kg CO_2 . Consumption of H_2O is 0.6429 kg.

The second final endothermic stage is described as



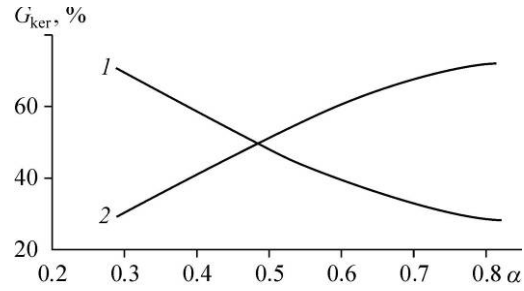
Being realized, this stage gives 0.3214 kg H_2 and 1.5 kg CO , consuming 0.9642 kg H_2O from 0.8571 kg CH_4 formed at the first stage of the steam reforming of 1 kg of kerosene.

Hence, the full steam reforming of 1 kg of kerosene results in 0.3214 kg H_2 , 1.5 kg CO , 0.7857 kg CO_2 , and 1.6071 kg H_2O is consumed.

To determine the kerosene flow rate for the steam reforming it was assumed that it had to correlate to the amount of the heat transferred through the heat-transfer wall from the combustion chamber when the gas in it was cooled down to $T_{c.c.}$ reached as the fuel was combusted at the specific oxidizer equivalence rate α , to the point $T_{m.a.}$ in the beginning of the mixture area of the gas jets coming from the combustion chamber and slit reactor. Meeting of this condition depends on the successful solution of the task related to the heat transfer from the combustion chamber through the heat-transfer wall for the steam reforming of the hydrocarbon fuel. Special experimental studies of the steam reforming of hydrocarbons were performed in the RSC "Applied Chemistry" to understand the implementability of this process; the goal was to choose the needed heat-proof material for the heat-transfer wall, and the optimal-type catalyst which would be able to provide the long converter life-time. These studies were carried out in experimental facilities with plasmatorches permitting to simulate any thermal conditions which could occur in the combustion chambers of the converters.

At the first stage of these experiments, steel 12Kh18N10T (Russian mark) was used as a material for the heat-transfer walls of model reactors; the maximum recommended temperature for this steel at the long-term operation is 600°C, whereas the oxidation scale starts to form in the air medium at 850°C [6]. According to the tests results, however, the 100% conversion of hydrocarbons under the conditions of the proposed converter model, it is necessary to have the heat-transfer wall temperature 900°C minimum. Thus,

Fig. 2. Flow rate percentage $G_{\text{ker.c.c.}}$ and $G_{\text{ker.s.c.}}$ versus α .
1 — $G_{\text{ker.c.c.}}$, 2 — $G_{\text{ker.s.c.}}$.



the heat-transfer walls material was replaced by the alloy of higher heat resistance, KhN78T (EI435), for which the recommended maximal temperature at the long-term utilization (10000 hours) in the air medium is 1100°C, the oxide scale formation starts at 1150°C [16]. Moreover, this alloy contains 78 % nickel which is used as an active component in catalysts. Later experiments proved the validity of this material.

For the thermodynamic investigations, the obtained experimental data were used to accept the temperature $T_{\text{m.a.}}$ in the beginning of the mixing area to be 1200 K.

At the same time, simultaneously with the above tests, different types of catalysts were tested. These experiments show that for the accepted thermal conditions of the steam reforming, the combination of pressed bars of nickel-chromium wire and of Al_2O_3 granules with Pt or Pd coating is optimal. Such a combination, when the kerosene steam reforming is organized properly, provides the full conversion, with no free carbon in the reaction products.

The amount of heat coming for the endothermic reaction of methane reforming in the slit reactor depends on the gas enthalpy difference ΔH in the combustion chamber, the enthalpies correlate to the temperatures $T_{\text{c.c.}}$ and $T_{\text{m.a.}}$. According to equation (2), the steam methane reforming needs $\Delta H_{\text{s.c.}} = 6058.82$ kJ/kg of the mixture. The value $\Delta H_{\text{s.c.}}$ dictates the amount of the methane-water mixture which must be supplied for absorption of the heat coming from the combustion chamber and corresponding to the ΔH obtained in the thermodynamic calculation.

Thus, the amount of the steam-methane mixture in the slit reactor per 1 kg of combustion products must be:

$$G_{\text{CH}_4 + \text{H}_2\text{O}} = \Delta H / \Delta H_{\text{s.c.}} = \Delta H / 6058.82 \text{ kg.}$$

It follows from (2) that 1 kg of the steam-methane mixture contains 0.4706 kg CH_4 , and during the first stage of the steam reforming of 1 kg of kerosene, 0.8571 kg CH_4 is formed. So, per 1 kg of the kerosene-oxygen mixture coming into the combustion chamber, the following should be supplied for the steam reforming:

$$G_{\text{ker.s.c.}} = (\Delta H / 6058.82) (0.4706 / 0.8571) = 9.062 \cdot 10^{-5} \Delta H \text{ kg.}$$

The percentage of the kerosene coming into the combustion chamber ($G_{\text{ker.c.c.}}$) and for the steam reforming ($G_{\text{ker.s.c.}}$) was found with the obtained values of $G_{\text{ker.s.c.}}$, as well as with the kerosene and oxygen flow rates supplied into the combustion chamber, for specific values of α . The calculation results are presented in Table 1, Figure 2 shows the values $G_{\text{ker.c.c.}}$ and $G_{\text{ker.s.c.}}$ versus the assigned values of the coefficient α .

The results of the thermodynamic calculations presented in Table 1 and Fig. 2 prove that, as the coefficient α rises, starting from $\alpha = 0.5$, the kerosene flow rate for the steam reforming

Table 1

Temperature and specific enthalpy of the gas in the combustion chamber at various α and percentage flow rates of kerosene coming for thermo-oxidative and steam reforming

α	0.3	0.4	0.5	0.6	0.7	0.8
$T_{\text{c.c.}}, \text{K}$	1662	2363	3029	3384	3526	3568
$\Delta H, \text{kJ/kg}$	2415.36	3235.90	4428.51	5565.66	6550.77	7385.59
$G_{\text{ker.s.c.}}, \%$	69.25	58.98	47.86	39.34	33.13	28.53
$G_{\text{ker.c.c.}}, \%$	30.75	41.02	52.14	60.66	66.87	71.47

starts to exceed the flow rate supplied into the combustion chamber, and it rises continuously along with α .

One of the major parameters governing the efficiency of hydrocarbon fuel reforming processes is the composition of the products after the converter. Table 2 presents the results of the thermodynamic calculations for various α , the compositions of the thermo-oxidative conversion products and their mixtures with the steam reforming products at the converter mixing area inlet. It was assumed at the calculations that the syngas produced by the steam reforming, as well as the thermo-oxidative conversion products come into the mixing area with the same temperature $T_{m.a.} = 1200$ K. Figure 3 shows the volume concentrations of hydrogen $x_{H_2c.c.}$ and $x_{H_2m.a.}$ versus the assigned values of α ; the dependencies are plotted with the data given in Table 2. It is evident from this Table that the kerosene conversion at $\alpha < 0.5$ in the mixing area would result in free carbon (soot) occurrence, which is extremely undesirable for the conversion products. Free carbon occurs in the converters with water-cooled walls, in low-temperature areas, especially on wall surfaces and in the near-wall layer. In this respect, thermodynamic investigations of the processes occurring in the near-wall layer of the combustion chamber were performed; they showed that, as the heat-transfer wall temperature was 1200 K and $\alpha \geq 0.5$, free carbon occurrence is excluded, not only in the near-wall layer, but also on the wall. This is proven by the data presented in Table 3.

The results of the performed thermodynamic investigations permit to make the following basic conclusions

1. Comparing to the convenient converter model where the only process of kerosene thermo-oxidative conversion is implemented in the regime with $\alpha = 0.3$, which corresponds to the maximal hydrogen content in the syngas, the converter of the proposed model always shows increasing hydrogen concentration at any regime, with α rising from 0.3 to 0.8, and

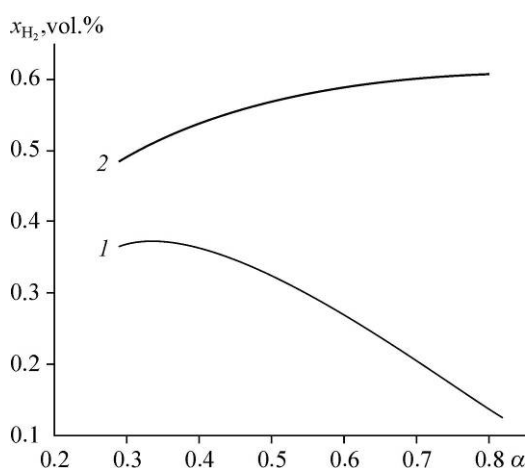


Fig. 3. Volume concentrations of hydrogen $x_{H_2c.c.}$ and $x_{H_2m.a.}$ versus the assigned values of α .

1 — $x_{H_2c.c.}$, 2 — $x_{H_2m.a.}$

Table 2

Mole fractions of the thermo-oxidative conversion products ($x_{c.c.}$) and mixture of the steam reforming products and thermo-oxidative conversion products ($x_{m.a.}$) in the mixing area for various α

α	0.3	0.4	0.5	0.6	0.7	0.8
$x_{H_2c.c.}$	0.3648	0.3621	0.3278	0.2679	0.1996	0.1302
$x_{H_2m.a.}$	0.4909	0.5374	0.5676	0.5867	0.5986	0.6108
$x_{COc.c.}$	0.3294	0.4302	0.3861	0.3211	0.2489	0.1694
$x_{COm.a.}$	0.2913	0.3244	0.2839	0.2531	0.2348	0.2218
$x_{CO_2c.c.}$	0.0485	0.0722	0.1249	0.1896	0.2624	0.3413
$x_{CO_2m.a.}$	0.0594	0.747	0.0933	0.1050	0.1238	0.1154
$x_{Cc.c.}$	0.1339	0.0092	0	0	0	0
$x_{Cm.a.}$	0.0824	0.0042	0	0	0	0
$x_{H_2Oc.c.}$	0.0733	0.0831	0.1451	0.2164	0.2886	0.3589
$x_{H_2Om.a.}$	0.0451	0.0390	0.0496	0.0540	0.0542	0.0520
$x_{CH_4c.c.}$	0.0502	0.0433	0.0162	0.0049	0.0012	0.0002
$x_{CH_4m.a.}$	0.0309	0.0203	0.0056	0.0012	0.0003	0

Table 3

Mass fractions of free carbon g_C in the converter combustion chamber at various gas temperatures T_g
for $\alpha = 0.5$ and gas pressure 20 atm

T_g, K	300	400	500	600	700	800	900	1000	1100	1200
g_C	0.2369	0.2368	0.1608	0.1394	0.1242	0.1119	0.0956	0.0628	0.0020	0

the hydrogen concentration 28–42 % above the maximum value in the thermo-oxidative conversion products at $\alpha = 0.3$. This process is illustrated in Fig. 3.

2. As the coefficient α rises in the converter combustion chamber with the separated fuel supply for the thermo-oxidative and steam reforming at the heat-transfer wall temperature of 1200 K, the fuel shares for the steam reforming at $\alpha = 0.5$ and for the thermo-oxidative conversion become equal. Further increase of α and retaining temperature of the heat-transfer wall at the level of 1200 K, the fuel share for the steam reforming rises significantly and reached 70% from the total kerosene flow rate supplied into the converter at $\alpha = 0.8$.

3. According to the results of thermodynamic investigations, in the regimes with $\alpha \geq 0.5$, when the heat-transfer wall is heated up to 1200 K, no free carbon (soot) occurs in the near-wall area or on the wall.

4. High degree of endothermicity of the kerosene steam reforming permits using this process to organize the regenerative system of cooling of the combustion chamber walls without heat loss into the ambient medium; in the case of walls water cooling, these heat losses would result in the significant decrease of the efficiency of fuel chemical energy transformation into the useful effect.

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